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**PITTING OF PICKERING NGS
UNITS 1 AND 2 PRIMARY HEAT
TRANSPORT SYSTEM - A PRELIMINARY
ASSESSMENT OF PIT GROWTH AND ITS
CORROSION IMPLICATIONS**

Report No 86-163-K

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ABSTRACT

An assessment has been made of the probability of further pit growth in the carbon steel feeders and martensitic stainless steel end fittings of Pickering NGS (PNGS) Unit 2 (pits were observed after its April 1984 decontamination). Field pitted and artificially pitted specimens were exposed for three months in a static LiOH solution having a typical CANDU primary heat transport system (PHTS) pH of 10.5 and a temperature of 300°C. In this test, pits did not grow in size within experimental uncertainties. A survey of the literature found no relevant pit propagation rates of carbon steel and martensitic stainless steels under similar PHTS conditions. However, literature data on the pitting properties of carbon steels suggest that the synergistic effects of PHTS solution chemistry and flow could cause pits with undercuttings and/or deposits to grow further during reactor shutdown and/or power operation. It is suggested that the probability and significance of such growth be further quantitatively determined.

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The possibility that other alloys in the PHTS may have been pitted during the April 1984 decontamination of PNGS Unit 2 has been evaluated. It was found that 17-4 PH alloys and leaded bronze could have been pitted in the low pH excursion during this decontamination.

The corrosion implications of PHTS pitting and possible secondary localized corrosion resulting from the pitting are presented.



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EXECUTIVE SUMMARY

PITTING OF PICKERING NGS UNITS 1 AND 2
PRIMARY HEAT TRANSPORT SYSTEM - A PRELIMINARY
ASSESSMENT OF PIT GROWTH AND ITS CORROSION IMPLICATIONS

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Pitting corrosion has been found in the carbon steel feeders of Pickering Units 1 and 2 (P1, P2) and the martensitic stainless steel end fitting and end fitting liners of P2, due probably to the high temperature decontamination of P1 in 1981 and the low pH excursion in the decontamination of P2 in 1984. This work attempts:

- to assess whether the existing pits will grow further under power operating conditions,
- to evaluate the possibility of pitting in other alloy components in the primary heat transport system (PHTS) of P2 due to the 1984 decontamination, and
- to recommend further work, if necessary, to address uncertainties and concerns with regard to pit growth and corrosion implications due to decontaminations raised in this project.

To obtain a preliminary set of data to assess the possibility of further pit growth in carbon steel and martensitic stainless steel, short term tests in static autoclaves and a literature survey were performed. To evaluate the possibility of pitting in other PHTS materials, tests were performed in a low pH decontamination solution to compare the pitting susceptibility of a number of representative PHTS materials to carbon steel and martensitic stainless steel which are known to pit in the test solution. In addition, a scope of the pitting problem, other possible forms of localized corrosion resulting from decontaminations and further work are presented. The following are findings in this project:

job	file	date	report no.
740682-177-50451	827.29	September 2, 1986	86-163-K

1. After three months in a static pH 10.5 LiOH solution at 300°C, pits in field pitted and artificially pitted specimens of a feeder, an end fitting, and an end fitting liner did not significantly change in size within experimental uncertainties.
2. There is no directly relevant data in the literature on the pit propagation rates of carbon steels and martensitic stainless steels in similar PHTS conditions.
3. Literature data on the pitting properties of carbon steels suggest that the synergistic effects of PHTS solution chemistry and flow could cause pits with undercuttings and/or deposits to grow further during reactor shutdown and/or power operation. Further work is required to determine the probability and significance of such growth.
4. The judged probability of stress corrosion cracking and corrosion fatigue resulting from the pits is low. Corrosion fatigue is more likely to initiate from the pits than stress corrosion cracking. As the pit size increases, the probability of crack initiation from the pits will increase.
5. In a pH 1.6 decontamination solution with a composition similar to that of the April 1984 P2 decontamination, 17-4 PH, nickel plated 17-4 PH, malcomized 17-4 PH and leaded bronze were pitted. Except for malcomized 17-4 PH, the severity of pitting is less than that of carbon steels and martensitic stainless steels. It is possible that P2 PHTS components made of these materials are also pitted.
6. In a potentiodynamic polarization test, Monel 400 and Inconel 600 were corroded intergranularly in a pH 2.6 decontamination solution. As intergranular attack is often a precursor of stress corrosion cracking, further work is recommended to determine the probability and conditions of such occurrence.

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TABLE OF CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
1.1 Statement of the Problem	1
1.2 Objective and Approach	2
2.0 PITTING OF CARBON STEEL AND MARTENSITIC STAINLESS STEEL	2
2.1 Alkaline Media	3
2.2 High Purity Water	5
3.0 PIT PROPAGATION TEST	5
3.1 Experimental	6
3.2 Results	6
4.0 PITTING SUSCEPTIBILITY TEST	7
4.1 Experimental	8
4.1.1 Immersion Test	8
4.1.2 Cyclic Potentiodynamic Polarization	8
4.1.3 Test Evaluations	8
4.2 Results	9
5.0 DISCUSSION	9
6.0 CONCLUSIONS	12
7.0 RECOMMENDATIONS	13
8.0 ACKNOWLEDGEMENT	16
REFERENCES	17
APPENDIX 1 - MORPHOLOGY OF PITS IN FEEDERS AND END FITTINGS	19
APPENDIX 2 - PRIVATE COMMUNICATIONS	20
APPENDIX 3 - APPEARANCE OF SPECIMENS AFTER PITTING SUSCEPTIBILITY TEST	23



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PITTING OF PICKERING NGS UNITS 1 AND 2 PRIMARY HEAT TRANSPORT SYSTEM - A PRELIMINARY ASSESSMENT OF PIT GROWTH AND ITS CORROSION IMPLICATIONS

1.0 INTRODUCTION

1.1 Statement of the Problem

Pitting corrosion was first observed in sections of a feeder and a grayloc hub removed from the primary heat transport system (PHTS) of Pickering NGS Unit 2 after its April 1984 decontamination/1/. Subsequent examinations of all feeder samples removed from Pickering NGS Units 1 and 2 (P1, P2) found that they were all pitted to some extent/2/. These feeders had experienced decontamination and/or the August 1983 P2 G16 pressure tube failure. Those that had experienced the low pH excursion of the April 1984 P2 decontamination or the high temperature decontamination of P1 in November 1981 were found to be more severely pitted than those that had not experienced either of these decontaminations.

Besides the carbon steel feeders, pits were also observed in some samples of P2 martensitic stainless steel end fittings and end fitting liners which had been decontaminated/3/.

The morphologies of these pits have been described in detail/2/ and a summary is given in Appendix 1.

Will these pits grow further under reactor operating conditions? Are other alloy components of PHTS which have not been inspected also pitted? These are the questions of concern to the long term integrity of the PHTS. The judgments at Ontario Hydro Research are that the probability of excessive additional pit growth in feeders and end fittings is low and that it is possible that pits are present in other PHTS alloy components. However, it is also recognized that Ontario Hydro has no direct, relevant experience or data on pitting in the PHTS, nor on the influence

of reactor operation on pit propagation, and thus, the corrosion implications of these pits are not precisely known. To address the lack of data, pitted specimens of feeders and end fittings have been placed in Pickering Unit 4 autoclaves. In addition, short term laboratory testing and a literature survey as described in this report were requested by Central Nuclear Services so that a scope of the problem could be provided and further work, if necessary, could be suggested to address any concerns.

1.2 Objective and Approach

The objectives of this project were:

- To assess the probability of additional pit growth and provide preliminary data on the rate of propagation in feeder and end fitting materials.
- To assess PHTS materials with respect to their susceptibility to pitting under simulated April 1984 low pH Pickering Unit 2 type decontamination conditions.

The project consisted of three parts.

1. Survey of literature on the pit propagation in feeder and end fitting materials under relevant reactor conditions and discussion with people working in the area.
2. Measurement of pit propagation rates of field and artificially pitted carbon and stainless steels in a pH 10.5 lithium hydroxide solution at PHTS operating temperature for a duration of approximately twelve weeks.
3. Performance of potentiodynamic polarization and immersion tests in decontamination solution to compare the pitting susceptibility of a selected number of PHTS materials to carbon steel.

2.0 PITTING OF CARBON STEEL AND MARTENSITIC STAINLESS STEEL

A literature search on the corrosion of carbon and stainless steels in high temperature waters turned up approximately twenty relevant papers and reports. Most of these papers reported on corrosion studies performed in high purity waters simulating the conditions of boiling water reactors. Papers reporting on studies performed in alkaline media were mostly focused on the properties of the corrosion product. None were devoted to pit propagation, nor did any address primarily the corrosion of martensitic stainless steel.

In general, at $\sim 300^{\circ}\text{C}$, carbon steel does not pit in high purity water containing up to several ppm of oxygen. Also, it does not pit in alkaline solutions having a $\text{pH} < 14$ in the absence of oxygen. When oxygen or a driving force that could raise its corrosion potential is present in the alkaline solution, carbon steel can pit. As the temperature of the test environment decreases, the pitting tendency of carbon steel increases regardless of the oxygen content or the alkalinity of the test media.

Only a few tests were reported in the literature on the corrosion of martensitic stainless steels at 300°C . From these few tests, it appears that martensitic steels do not pit in alkaline solution containing up to several hundred ppb of oxygen, but galvanic effects may cause pitting at lower temperatures. In high purity water, contradictory results on the occurrence of pitting were reported.

Dynamic solution flow appears to have an influence on the initiation of pits in these steels but its overall effect is not clear.

Besides surveying the literature, attempts were made to solicit pit propagation rates from a number of corrosion engineers and metallurgists who are working or have experience in the corrosion of reactor materials. They included engineers and scientists from Atomic Energy of Canada Ltd (AECL), Brookhaven National Laboratory (BNL), Central Electricity Generating Board (CEGB), Central Thermal Services (CTS), Northeast Utilities, Ohio State University (OSU), Virginia Power Corporation and Westinghouse Canada Inc. None of them had any data on pit propagation rates in carbon or martensitic steels at high temperatures. On the whole, their views agree with thinking at Ontario Hydro Research and also literature results. They commented that carbon steel does not generally pit in the PHTS environment and consequently, existing pits are unlikely to grow. Some stressed the importance of chemistry control and some cautioned that shutdown conditions, dynamic solution flow and galvanic coupling may cause further pit growth. These private communications are reported in Appendix 2.

The following subsections present the findings of the literature review in more detail.

2.1 Alkaline Media

In the late 1960's, Canadian Westinghouse performed a series of corrosion tests for AECL on a number of CANDU PHTS materials, which included A106 carbon steel and 410 stainless steel/4,5/. The tests were conducted in a dynamic loop with a flow rate of 6 m/s at 293°C and also in autoclaves at 65°C and 149°C .

However, not all of the materials were tested at all three temperatures. The test medium was a pH 10 LiOH solution with an oxygen concentration of either <5 ppb or ~200 ppb. The duration for each test was ~1 y. In the solution with <5 ppb oxygen, carbon steel was tested only at 293°C. Pitting was not observed. In the solution with ~200 ppb oxygen, it was pitted at all three temperatures. The pits were larger at the lower temperatures and appeared to lie in the direction of flow in the loop. Type 410 stainless steel was not pitted in either solution at all three temperatures. However, when coupled with cast steel in the solution with the lower oxygen content, it was pitted at the two lower temperatures.

Other high temperature studies on carbon or mild steels in alkaline solutions were carried out in solutions without de-aeration and they focused mainly on the oxide film or corrosion product. One finding of interest from some of these studies/6,7,8,9/ was that there is no major difference in the morphology and composition of the oxide films grown in NaOH and in LiOH solutions with a pH <~14. Another finding of interest is that the corrosion rates of carbon and mild steels in static alkaline solutions decrease with time and after ~25 days, increase monotonically with pH. However, in dynamic systems, there were reports/10,11/ on rate decrease with an increase in pH.

None of these high temperature studies in alkaline solutions with a pH <~14 mentioned whether pitting was observed. Presumably, pits did not appear. However, the possibility that pits could be initiated in these solutions was implicated in a potentiostatic study of a mild steel in NaOH solutions having concentrations of from 0.0016 N to 5 N/12/. In solutions having a pH >12, pitting did not appear at applied potentials up to the anodic limit of oxygen evolution, but in solutions having a pH <12, pitting occurred at potentials >800 mV vs a 304 stainless steel reference electrode. Consistent with the above implication were observations from a study on the effects of heat transfer on the corrosion of carbon steel in boiling (~100°C) NaOH solutions having concentrations of 0.1 N, 1 N and 5 N/13/. In a 4 day test, pits were not observed in samples with or without an applied heat flux immersed in a 5 N NaOH solution but in 1 N and 0.1 N NaOH solutions, when a heat flux of ~3 x 10⁵ kcal/m².h was applied, pits appeared.

The observation that pitting did not appear in solutions with a high alkali concentration at high temperatures is valid only in tests with a short duration. In tests with longer durations, pits were observed in mild and carbon steels in 4 N and 10 N NaOH solutions at 315°C/14,15/. In a 4 N NaOH solution, pits were observable after 68 days of testing/15/. Though pit propagation rate had not been mentioned in the report, it could

be estimated from the cross sections of the pits shown. After ~1 y, the pit depths were ~100 μm .

2.2 High Purity Water

Recently, a detailed study has been performed on the corrosion of SA106 carbon steel in high purity water with oxygen contents varying from 0.02 ppm to 8 ppm and at temperatures varying from 50°C to 288°C/16,17/. During a test duration of 200 h, pitting did not occur in any of the oxygenated test waters at 288°C and in water containing 0.02 ppm of oxygen at any test temperatures. Within the constraint of the test parameters, pits only began to appear at an oxygen concentration of 1 ppm at temperatures below 175°C. This agrees with an earlier study/18/ in which pitting was not observed in iron after 1500 h at 240°C to 360°C in water with <0.15 ppm of oxygen. It appears that increasing the oxygen content of the water will require a higher temperature to prevent the occurrence of pitting.

The above work complements a study/19/ performed on the corrosion of iron in waters containing higher oxygen concentrations of 35 ppm to 540 ppm. At 35 ppm of oxygen, iron was pitted at all test temperatures from 50°C to 315°C in a test duration of three days. However, increasing the oxygen concentration further would begin to produce a protective oxide film on the iron surface at the higher temperatures and pitting ceased to appear. Pitting of carbon steel in water containing <1 ppm of oxygen at 315°C was reported by two earlier studies/20,21/. However, unlike the above mentioned investigations, these studies were carried out in test loops with dynamic solution flows. In one study using a loop with a flow rate of ~9 m/s and an oxygen concentration of ~0.6 ppm, both carbon steels and martensitic stainless steels were classified as having a low corrosion resistance/20/. This classification was due to the observation of heavy deposits of corrosion products or deep pitting on the steels. In the other study, steels containing up to 5% Cr showed similar corrosion behaviour with some pitting or localized attack in tests lasting from 3 to 84 days at a flow rate of ~1.8 m/s and dissolved oxygen content from 0.08 to 0.1 ppm/21/. The size of the attack did not appear to increase with time. Localized attack did not occur on 304 and 410 stainless steels.

3.0 PIT PROPAGATION TEST

To generate some data on the propagation rates of pits in carbon and martensitic steels in an environment similar to the PHTS, pitted coupons were tested in a de-aerated pH 10.5 LiOH solution at 300°C for approximately 3 months in static autoclaves.

3.1 Experimental

The coupons used in the test were made of carbon steel, 403 stainless steel and 410 stainless steel. Three sets of samples were tested, each consisting of one coupon each of the different materials. In one set, actual field pitted samples were used. No pretreatment, other than laboratory decontamination, was performed on these samples, which retained a layer of corrosion product. The pits in this set had average depths of 212 μm on carbon steel, 35 μm on 403 stainless steel and 30 μm on 410 stainless steel. The other two sets of samples were finished with a 120 grit paper and artificially pitted by passing an anodic current through pinholes in its wax covered surface in a 1 N HCl solution. The wax was subsequently removed from the sample before testing. The pits in one of these two sets had average sizes approximating those of the field pitted samples; 280 μm deep on carbon steel, 35 μm on 403 stainless steel and 49 μm on 410 stainless steel. The other set had much smaller pit depths. They were 14 μm on carbon steel, 13 μm on 403 stainless steel and 9 μm on 410 stainless steel.

The pit depths reported here were measured with an optical microscope by focusing on the top and bottom of the pit and noting the readings of a calibrated focusing dial. The instrument precision is better than 2 μm . However, focusing error could reduce the precision of the method. The identities and positions of the measured pits were recorded and photographed. The photographs also served to compare the appearances of the coupons before and after test.

The 4 L autoclaves used in the test had carbon steel liners which had been preconditioned at 300°C in a test solution for a day. One set of samples occupied one autoclave containing 1.5 L of the de-aerated test solution. The autoclave used for the field pitted samples also contained a set of pitted feeder specimens which had previously been installed in Pickering Unit 4 autoclaves. The circumstances of this set of samples will be reported by the Chemical Research Department.

3.2 Results

The pH of the test solution was measured at room temperature. It had a pH of 10.5 before test and ~8.5 after test, or ~0.45 mmol of hydroxide was consumed. The cause of the decrease in pH was not investigated. It could be due to:

1. adsorption of hydroxide ion on the carbon steel autoclave liner and test coupons
2. corrosion of the liner and test coupons and/or

3. hydrolysis of the corrosion products on the line and test coupons.

After test, there was no apparent change in the appearance of the artificially pitted coupons but a slight deposit on parts of the field pitted samples.

Table I shows the average pit depths measured before and after the test. Within experimental uncertainties, the pits did not appear to change in size.

TABLE I
PIT DEPTHS FROM AUTOCLAVE TEST
(pH 10.5 LiOH, 300°C)

Run No.	Pitting Source	Duration (Days)	Material	Number of Pits	Average Pit Depth (μ m)	
					Before Test	After Test
1	field pitted	104	C-Steel	5	196 $\pm$ 39	195 $\pm$ 24
			403SS	3	35 $\pm$ 5	35 $\pm$ 5
			410SS	1	30	30
2	artificially pitted	84	C-Steel	11	280 $\pm$ 240	267 $\pm$ 236
			403SS	11	36 $\pm$ 12	34 $\pm$ 7
			410SS	11	49 $\pm$ 16	53 $\pm$ 20
3	artificially pitted	90	C-Steel	11	14 $\pm$ 5	14 $\pm$ 5
			403SS	10	15 $\pm$ 4	15 $\pm$ 4
			410SS	11	9 $\pm$ 4	9 $\pm$ 4

*Note: pit depth $\pm$ 1 standard deviation

4.0 PITTING SUSCEPTIBILITY TEST

To provide an indication of what other materials in the PHTS could possibly have been pitted during the low pH excursion of

the April, 1984 P2 decontamination, two tests, an immersion test and a cyclic potentiodynamic polarization test, were performed.

4.1 Experimental

The test materials, representing the different types of alloys which could have been decontaminated in the PHTS, included A105 carbon steel, 403 stainless steel, 410 stainless steel, 17-4 PH stainless steel, nickel plated 17-4 PH, malcomized 17-4 PH, leaded bronze, Monel 400, Inconel 600, Stellite 6, custom 455 stainless steel and 304 stainless steel. Type 403, 410, 17-4 PH and custom 455 stainless steels were supplied by Pickering NGS. The nickel plating and malcomizing of 17-4 PH were performed by local companies. Stellite 6 was welded on a piece of carbon steel at Research. The rest of the materials were samples stocked at Research obtained from various sources. The composition of these materials, except those from the station, could be supplied on request. The finish on the test materials was 600 grit.

The compositions of the test solutions were similar to that of the low pH excursion of the April 1984 P2 decontamination. A liter of the solution contained up of 600 mg of EDTA, 200 mg of citric acid, 50 mg of oxalic acid and 50 mg of Rodine 31A. The pH of the solution was ~2.6. The solution was de-aerated with nitrogen and held at 85°C during tests.

4.1.1 Immersion Test

In the immersion test, the pH of the solution was further adjusted to 1.6 with sulphuric acid. At this pH, both carbon and martensitic steels have been shown to pit/2/ and thus, solutions with this pH were used to facilitate the comparison of the pitting characteristics of the different materials. The duration of the exposure of the materials was ~3.5 h.

4.1.2 Cyclic Potentiodynamic Polarization

In the cyclic potentiodynamic polarization test, at a scan rate of 1.2 V/h, the specimen was polarized anodically from its corrosion potential to 1.6 volt vs a calomel reference electrode and then returned to its corrosion potential, thus forcing the specimen through a range of oxidizing conditions in a single test solution. The methodology and instrumentation of the test is given in ASTM G5.

4.1.3 Test Evaluations

After both tests, the specimens were examined microscopically to determine the form and severity of corrosive attack.

4.2 Results

Alloys 17-4 PH, nickel plated 17-4 PH, malcomized 17-4 PH, leaded bronze, 403 stainless steel, 410 stainless steel and A105 carbon steel were pitted in the immersion test as well as in the cyclic potentiodynamic polarization test. Pits in leaded bronze and the 17-4 PH alloys, except malcomized 17-4 PH, were much smaller and less dense than those in the martensitic and carbon steels. Malcomized 17-4 PH had pits which could be grouped into two sizes. Pits of one group were much smaller and of the other were larger than those of the martensitic and carbon steels. Inconel 600 and Monel 400 had pit initiations from the immersion test but intergranular attack (IGA) from the potentiodynamic polarization test. None of the other alloys, Stellite 6, 304 and Carpenter 455 stainless steels, showed any sign of pitting attack. Carpenter 455 and 304 stainless steels were slightly tarnished whereas Stellite 6 showed general dendritic corrosion in the potentiodynamic polarization test.

The results of the tests are shown in Table II and pictures of the appearances of the specimens are given in Appendix 3.

5.0 DISCUSSION

Results of the short-term autoclave tests showed that within experimental uncertainties, there was no significant change in the sizes of pits in both field pitted and artificially pitted carbon steel and martensitic stainless steel. However, because of the limitations of the test equipment, a stable pH was not maintained and solution flow, which probably played a role in the pit initiation of feeders and end fittings/2/, was not simulated.

Unfortunately, there was no study reported in the literature investigating pit propagation of carbon and martensitic steels under directly relevant PHTS or similar chemical and temperature conditions, let alone data on the effects of hydrodynamics on pit growth. This is expected because pits do not generally initiate in such an environment/4/. There were, however, observations of pitting in carbon steels in high purity water in a dynamic flowing system/21/ but not in a refreshed system/16,17,18/. Although this suggests that solution flow could assist in the initiation of pits, the synergistic effects of solution flow and other environmental conditions on pitting cannot be established from this work. At $\sim 300^{\circ}\text{C}$, in a dynamic flowing pH 10 LiOH

TABLE II
PITTING SUSCEPTIBILITY OF PHTS MATERIALS
IN A DECONTAMINATION SOLUTION¹

MATERIAL	OBSERVATIONS ²	
	<u>Immersion Test³</u>	<u>Potentiodynamic Test⁴</u>
304SS	clean surface	tarnished surface
455SS	tarnished surface	tarnished surface
Stellite 6	tarnished surface	dendritic corrosion
I600	pit initiation	IGA
M400	pit initiation	IGA
Ni plated 17-4 PH	pit initiation	a few pits (~4 μ m)
17-4 PH	a few pits (<2 μ m)	a few pits (<2 μ m)
leaded bronze	a few pits (4-8 μ m)	rough surface, pits
malcomized 17-4 PH	a few pits (~2 μ m, 45-80 m)	rough surface, pits
403SS	pits (~20 μ m)	pits (2-5 μ m)
410SS	pits (~60 μ m)	pits (3-10 μ m)
A105CS	pits (~40 μ m)	rough surface, pits

NOTES:

1. 1 kg contains 600 mg EDTA, 200 mg citric acid, 50 mg oxalic acid and 50 mg Rodine 31A; pH adjusted by sulphuric acid.
2. Pit depth measurement in bracket.
3. pH = 1.6, test duration = 3.5 h.
4. pH = 2.6, scan rate = 1.2 V/h, potential range = cyclic scanning from corrosion potential to 1.6 V vs saturated calomel electrode.
5. IGA = intergranular attack.

solution with 200 ppb of oxygen, carbon steel pitted/5/, while in the same system with <5 ppb of oxygen/4/, and also in continuously refreshed high purity water with 200 ppb of oxygen, carbon steel did not pit/16,17,18/. It seems that for a given flow rate, increasing the oxygen content of the medium could increase the tendency of pit initiation in carbon steel, and that for a given oxygen content, increasing the flow rate and/or pH could also increase the pitting tendency. It is possible that such interactions could also apply to pit growth. Indeed, in a static 15% NaOH solution at 315°C, pits appeared in carbon steel in 68 days/15/ and after a year, grew to a depth of ~100µm. This lends support to the possibility that pits could grow in an alkaline medium at high temperature. Further, the type of pits with an undercut found in the feeders and the subsurface pits found in the end fittings are known to be most prone to pit growth in other environments. Thus, the possible growth of an oxide film in the pits at reactor operating temperature may not be protective under dynamic flow and/or its interactions with variations in the oxygen content, pH or other impurities such as cuprous, cupric and ferric ions in the PHTS. The probability of these interactions causing rapid pit growth may be small but its assessment must await further experimentation.

Aside from our small, but non-negligible concern of further pit growth under reactor operating conditions, data in the literature have indicated that the pitting tendency of carbon steel increases as temperature decreases regardless of the oxygen content and pH of the environment/5,16/. Also, at lower temperature, martensitic stainless steels were pitted when coupled with cast steels/5/. Thus, there is a potential for pit growth in carbon and martensitic steels during reactor shutdown and start up processes.

Besides further pit growth, other corrosion implications of the pits, such as, stress corrosion cracking and corrosion fatigue initiating from pits, have been considered/Appendix 2/.

Stress corrosion cracking in carbon steel in high temperature water is unlikely; however, relevant data are limited and the possible consequences are potentially significant. There are only two studies reported in the literature dealing with this topic/16,22,23/. Both found that stress corrosion cracking of carbon steel should not be a problem in high purity water. However, these studies used samples without an existing flaw. The existence of pits could lead to local environmental and mechanical conditions conducive to crack initiation. The effect of raising the pH of the solution on stress corrosion cracking at high temperatures is also unclear. As for martensitic stainless steel, one study/18/ reported an observation of cracking on a specimen of AISI 431 (tempered at 371°C) in a

285°C water with ~0.1 ppm of oxygen. It is believed that stress corrosion cracking on martensitic stainless steels can be prevented by tempering it at a higher temperature (eg, ~600°C).

Corrosion fatigue is a process similar to stress corrosion in which a combination of corrosion and cyclic stress causes cracking to occur. There is little information on its initiation and the crack propagation rate is complicated dependent on a number of factors such as the load waveform, load amplitude, loading frequency, solution composition and solution flow rate. Corrosion fatigue initiating from pits in carbon steel is considered unlikely but more probable to occur than stress corrosion cracking. Worth mentioning are that one of the major causes of boiler failure in thermal plants is corrosion fatigue initiated from pits in carbon steel and that cases of cracking in steam generators in nuclear plants due to corrosion fatigue initiated from pits have been surfacing in recent years/Appendix 2/. Thus, the unlikelihood of its occurrence must also be confirmed.

From the tests performed on the pitting susceptibility of PHTS materials in low pH decontamination solutions, pits were observed in 17-4 PH, nickel plated 17-4 PH, malcomized 17-4 PH and leaded bronze. Though the pitting tendency of these materials appeared much less than that of carbon steel, 403 stainless steel or 410 stainless steel, they may have been pitted in the PHTS of P1 and P2. Also, coupling of two different metallic materials could affect their pitting susceptibilities. For example, in a de-aerated alkaline solution at low temperatures, martensitic stainless steel did not pit, but when coupled with cast steel, pitting occurred/4/. The effects of galvanic coupling on the pitting susceptibility of PHTS materials in decontamination solutions have not been examined and should be investigated.

In the potentiodynamic polarization test, intergranular attack was observed on I600 and M400. As intergranular corrosion is often a precursor of stress corrosion cracking, more elaborate tests must be performed to determine the conditions and severity of its occurrence.

Most decontamination studies in the past conducted at Hydro and AECL focused mainly on the role of the components of the decontamination solution on the decontaminability and corrosivity on carbon steel. Little is understood on the role of these components on other PHTS materials. Further study in this area would help in the understanding of the process.

6.0 CONCLUSIONS

Although tests in a static pH 10.5 LiOH solution at 300°C did not show any significant further pit growth in carbon steel and

martensitic stainless steel, analyzing literature data on their pitting properties in high temperature waters and the morphologies of pits found in the feeders and end fittings, it is judged possible that the synergistic effects of dynamic solution flow, oxygen and high pH could cause further pit growth in some of the pits in the feeders of P1 and P2. The probability of significant pit growth under such influences is not known due to a lack of data and thus requires further study.

Other situations which could possibly cause further pit growth are reactor shutdowns and start ups, and at locations where galvanic couplings could exert an influence. However, these situations have not been considered in detail in this project and should be further investigated.

The probabilities of stress corrosion cracking and corrosion fatigue initiating from pits in feeders are small but should be confirmed due to the possible significant implications of such occurrence.

Other materials in P2 which may have been pitted include alloys of 17-4 PH and leaded bronze. Monel 400 and Inconel 600 could be attacked by intergranular corrosion in decontamination solutions. The conditions under which this could happen need further investigation.

7.0 RECOMMENDATIONS

It is emphasized here that good water chemistry control must be exercised during reactor operation, shutdown and startup to control pitting in the PHTS of P2. The tolerances of the variations in water chemistry and its significance on further pit growth, if there is any, should be more quantitatively determined. Work should be performed to quantify the uncertainties concerning pit growth and its potential implications raised in this study. If possible, a nondestructive evaluation method should be developed to monitor pit depths in P2 feeders. In view of the observations of intergranular attack on Monel 400 and Inconel 600 from our tested low pH decontamination solution, the role of the reagents on the corrosion of PHTS materials should be further investigated.

In order to confidently, reliably and fully predict the potential for and implication of pitting in PHTS materials, the following work requires further elaboration:

1. Investigate the effects of solution chemistry, galvanic coupling, temperature and solution flow rate on further pit growth of carbon steel and martensitic stainless steel.

2. Investigate the effects of decontamination on the corrosion of M400 and I600.
3. Investigate the effects of galvanic coupling on the pitting susceptibilities of PHTS materials in decontamination solution.
4. Perform experiments to confirm the belief that stress corrosion cracking and corrosion fatigue are unlikely to initiate from pits in carbon steel and martensitic stainless steel under CANDU PHTS conditions.
5. Examine the effects of repetitive decontamination on pitting of carbon steel and martensitic stainless steel.

To carry out the above work in detail would require commitment of large resources which, in our opinion would not be cost effective, given the currently judged low risk. It is recommended here that work be carried out in planned stages with the work content of each stage adjusting to or depending on the results of the previous one. Short term tests using a few limiting conditions and/or analysis of available data could be performed as in the present study such that the scope of the problem could be redefined at the end of each stage. We recommend that further work be considered according to the following priorities:

1. Pit growth of carbon steel and martensitic stainless steel should continue to be monitored and evaluated by periodic removal of PHTS autoclave coupons or component samples as well as tests in laboratory autoclaves. Field experiments could provide information on the influence of actual solution chemistry on pit growth, while laboratory experiments could determine the relative contribution of each chemical to pit growth and the conditions under which pit growth could occur. The following laboratory experiments should be performed:
 - (i) Tests, each with a duration of at least 4 months, to determine the pit propagation of carbon steel and martensitic stainless steel in flowing as well as in continuously refreshing solutions having typical maximum concentration of cuprous, cupric, ferric and halide ions with typical concentration limits of oxygen and hydroxide ions in the PHTS at 300°C and 50°C.
 - (ii) Tests in the above solutions at temperatures cycling from 50°C to 300°C and then back to 50°C to evaluate if temperature shocks could cause pit growth.

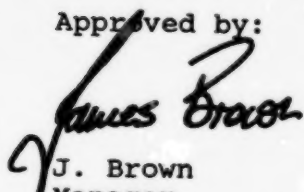
- (iii) As the next stage to the above work, tests at 300°C, and 50°C should be performed to determine the concentration limits of oxygen, cuprous, cupric, ferric, halide and hydroxide ions within which pit propagation could not occur.
2. Potentiostatic polarization as well as cyclic potentiodynamic polarization tests could be performed to determine the potential ranges where intergranular attack (IGA) could occur on Monel 400 and Inconel 600 in typical decontamination solutions. Further stages should determine the role of each decontamination component in the IGA of M400 and I600. This should involve electrochemical, immersion as well as loop tests such that the decontamination process could be improved.
 3. Immersion tests should be performed to determine if galvanic coupling could cause pitting in PHTS materials in low pH decontamination solutions.
 4. As a first stage to determine the possibility of stress corrosion cracking and corrosion fatigue initiating from existing pits in the PHTS, a literature survey could be performed to determine the scope of the problem. Pitted U-bend specimens could be tested for stress corrosion cracking in a pH 10.5 LiOH solution at 300°C. Constant extension rate tests should be performed at a later stage for a better evaluation. At present, Hydro Research does not possess equipment for testing corrosion fatigue in high temperature waters but a system is being acquired for thermal plant work. Negotiation could be made to borrow the system to perform nuclear plant work in the future.
 5. Measurement of changes in pit sizes in pitted specimens after a number of cycles in a typical decontamination solution, and at 300°C in a pH 10.5 LiOH solution should be the first stage to examine the effects of repetitive decontamination on pitting. Later stages could involve varying the limiting conditions of the solutions and should be performed in a dynamic test loop.

Works on pit growth and intergranular corrosion (1 and 2 above) should receive our first attention as P1 and P2 will be back in service soon. The initial stages of the proposed works would require ~2.5 years to complete. If excessive pit growth and intergranular corrosion is judged probable, the emphasis of work would probably shift to include stress corrosion cracking and corrosion fatigue. Work on the effects of repetitive decontaminations could be scheduled according to possible future consideration of decontamination of P1 and P2.

8. ACKNOWLEDGEMENT

The pit propagation and pitting susceptibility tests were performed by Laniel Grant and Bonnie Guest. The cooperation of Vivian Chew for use of an autoclave in the radioactive laboratory is appreciated. The pitting problem has been discussed with a number of metallurgists and corrosion scientists. Thanks to them.

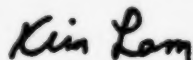
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Technology Section

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APPENDIX 1

MORPHOLOGY OF PITS IN FEEDERS AND ENDFITTINGS

The following is a summary of the morphology of the pits found in the PHTS. For a more detailed description, the original reports/1,2,3/ should be consulted.

The pits found in the feeders had depths ranging from 20 to 500 μm . Generally, the walls of the pits from P1 feeders were covered with an oxide layer of $\sim 10 \mu\text{m}$, which was approximately 7 to 10 times less than the oxide layer surrounding the pits. The pits from P2 feeders were in general filled with corrosion products and were either covered with a red oxide blister or a continuous oxide layer from the surrounding surface. The shape of the pits was in general hemispherical. Undercutting was observed in pits in a P2 outlet hub. The appearance of the pits in the P2 outlet hub and also in some of the P2 outlet feeders was oval or pear shaped with its length aligned in the direction of flow.

The size of the pits found in the end fitting bodies and liners was much smaller. The depth of pits ranged from ~ 20 to 45 μm . Pitting was in general subsurface or roughly $3/4$ of a sphere in shape. The pits on the liners appeared to line up in the direction of flow.

APPENDIX 2

PRIVATE COMMUNICATIONS

The pitting problem in the feeders and end fittings has been discussed with a number of corrosion engineers and metallurgists. They were asked for any relevant pit propagation data they had or knew of. Also, they were asked to give their opinion on the probability of further pit growth or on the corrosion implications of the pits on the system. As expected, none of them had any data on high temperature pit propagation rates in carbon steel or martensitic stainless steel but judged that any further pit growth would likely be minimal. The views of these experts are interpreted as follows:

1. George Taylor; AECL, Chalk River, Ontario.

No work has been performed on the corrosion of feeder and end-fitting materials in high temperature environments in AECL for the past 10 y. There were some corrosion tests on stainless steel in heavy water plant environments. In these tests, pits on the samples did not grow. The pits on feeders and end fittings probably will not propagate. Since there is no data in this area, it is difficult to state it with certainty.

2. Carl Czajkowski; BNL, Upton, New York.

Carl Czajkowski has performed a failure analysis on the 1982 cracking of the closure welds on the steam generators of Indian Point 3/24/. Corrosion fatigue initiated from pits was suggested as the cause of failure. As a follow-up to the Indian Point 3 investigation, he has performed a few stress corrosion cracking tests and generated some data on the cracking rate in carbon steel. He was understandably unwilling to disclose the test results before publication. However, he did mention that from his CERT tests, stress corrosion cracking is not likely to appear in carbon steel in high temperature alkaline solutions because the corrosion potential shifts out of the cracking potential region. He felt that similarly, pitting in carbon steel should not appear in high temperature alkaline solutions.

3. Allan Rantell; CEGB, Leatherhead, United Kingdom.

With good water chemistry, the pits should have no corrosion implication. Oxygen and halide concentrations must be strictly controlled. The possibility for stress corrosion cracking to occur is little and corrosion fatigue is more likely to occur than stress corrosion cracking.

4. Duncan Sidey, CTS.

Duncan Sidey talked mainly of his experience in thermal plants. The economizers of thermal plants have an environment close to that of the PHTS. It operates at a temperature of from 250°C to 300°C and a pH of ~9. Most failures of carbon steel components in thermal plants are due to corrosion fatigue. It is difficult to pinpoint the cause of corrosion fatigue and there is not a significant amount of information on crack initiation in boiler type water.

5. Michael Hudson, Northeast Utilities, Berlin, Connecticut.

Michael Hudson had performed a series of corrosion tests on PHTS materials at Canadian Westinghouse for AECL in the late 1960's. He cannot remember the results of the work which was done over 15 y ago but can remember there was a case of severe pitting in the grayloc seal caused probably by shutdown. He believes the pits in the feeders and end fittings will not propagate once the reactor is back to normal operation.

6. Zuzanna Szklarska-Smialowska; OSU, Columbia, Ohio.

Zuzanna Szklarska-Smialowska is one of the world's leading authorities in the field of pitting corrosion. She has done contract research for EPRI on pitting corrosion of carbon steel in high purity water. She avoided giving a definitive answer to the question of whether the pits will further propagate, but instead, pointed out factors which could cause further pit growth, stressed the importance of chemistry control and cautioned about shutdown which might cause pits to propagate. With the presence of any Cu^+ , Cu^{2+} , Fe^{3+} , Cl^- and O_2 , even at sub ppm levels, pits in carbon steel at high temperatures will grow. Galvanic coupling can cause further pit growth depending on the corrosion potentials of the coupled materials. The occurrence of stress corrosion cracking does not necessarily require very high stresses. It could occur in solutions with a $\text{pH} \geq 14$ at 50°C, and the pH limit requirement decreases with increasing temperature.

7. Joseph McAvoy; Virginia Power Corporation, Richmond, Virginia.

Virginia Power Corporation discovered cracking in the transition girth welds of all of its three Slurry-2 steam generators in 1983. Most of the cracks were initiated from pits in the vicinity of the welds. The pits were probably caused by bad water chemistry during 1973 to 1979 (very bad water chemistry after 1975) due to condenser leakages. Cracks of up to 1.3 cm were measured. Any measurements of changes in pit depth will take place in 2 y.

8. Norman Graham, Westinghouse Canada Inc., Port Hope, Ontario.

Pits will probably not grow further at normal operating conditions but the erosion-corrosion effects of solution flow to pitting could be a concern. The pits will probably grow during shutdown. Stress corrosion cracking of carbon steel at PHTS temperature is unlikely. Corrosion-fatigue is possible if there is a stress raiser.

APPENDIX 3

APPEARANCE OF SPECIMENS AFTER
PITTING SUSCEPTIBILITY TEST

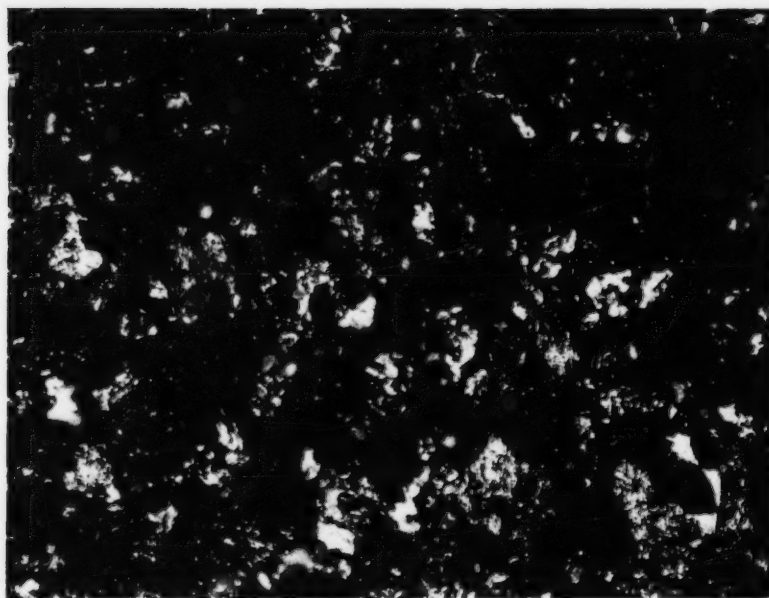


FIGURE A1

A105 CARBON STEEL AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

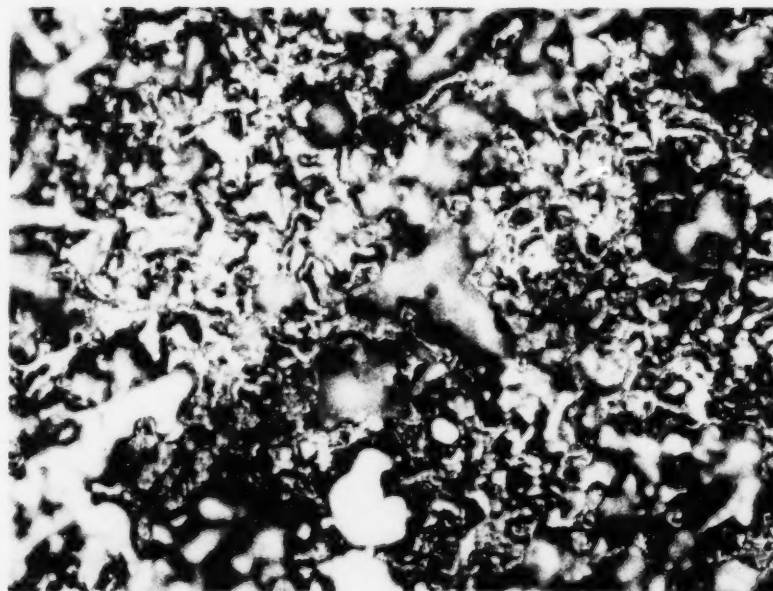


FIGURE A2

LEADED BRONZE AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

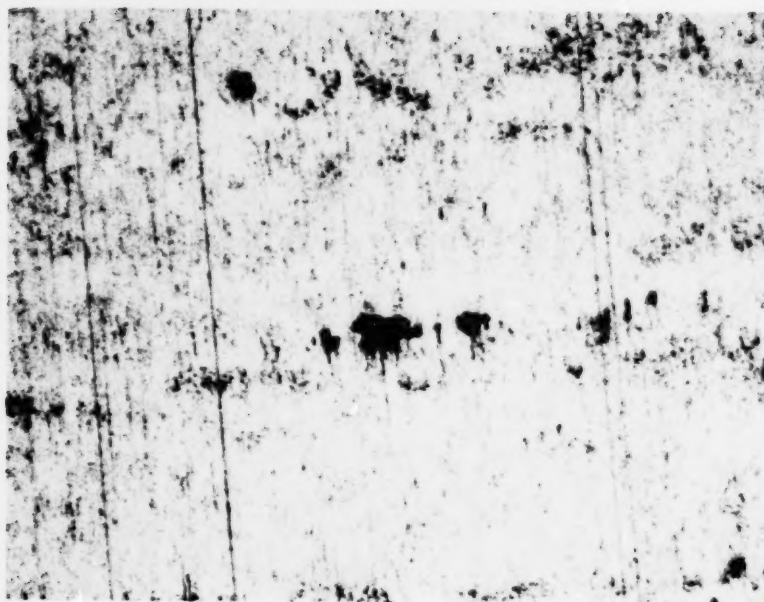


FIGURE A3

410 STAINLESS STEEL AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

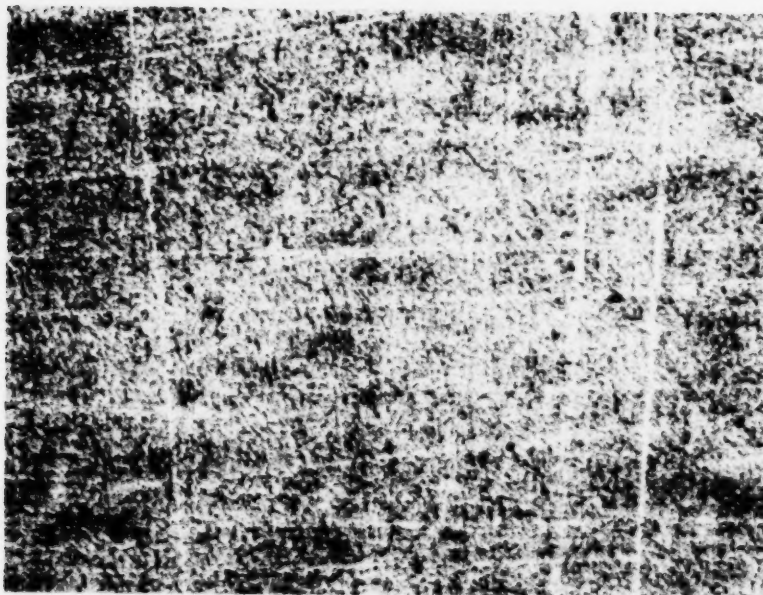


FIGURE A4

403 STAINLESS STEEL AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

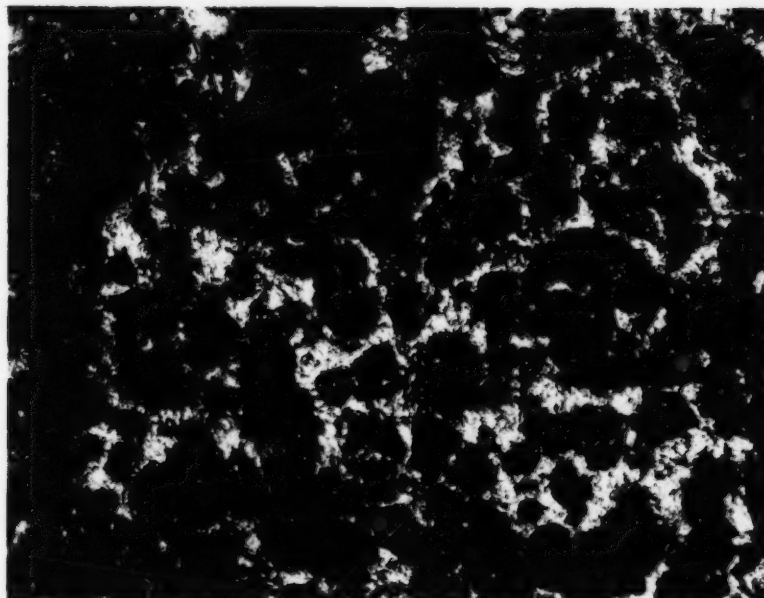


FIGURE A5

MALCOMIZED 17-4PH AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

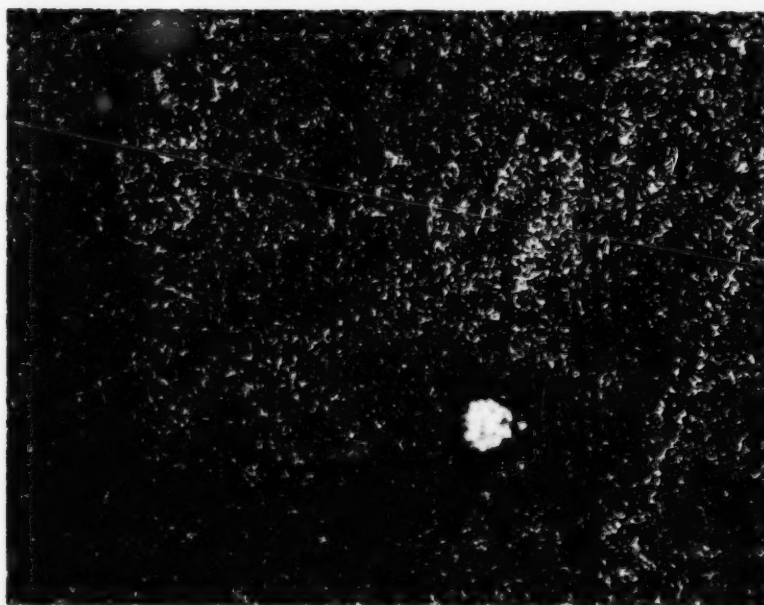


FIGURE A6

NICKEL PLATED 17-4PH AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)



FIGURE A7

ALLOY 17-4PH AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

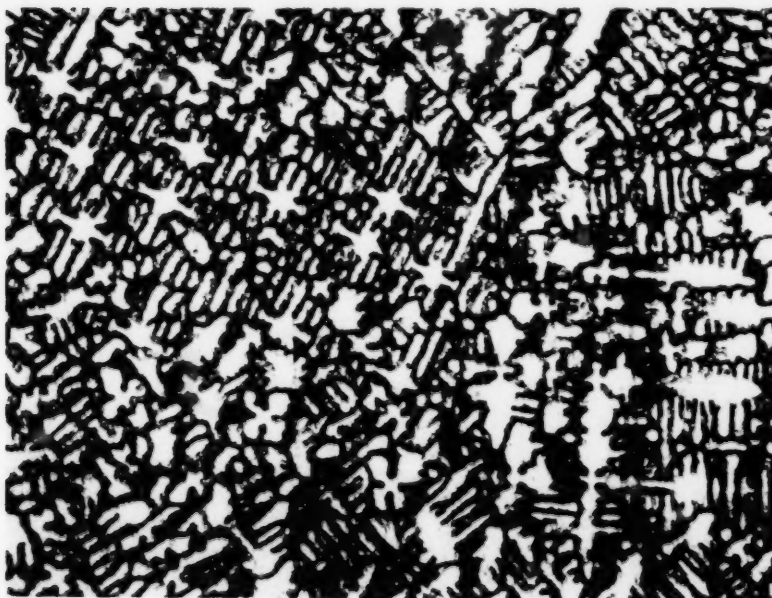


FIGURE A8

STELLITE 6 AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)



FIGURE A9

MONEL 400 AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)

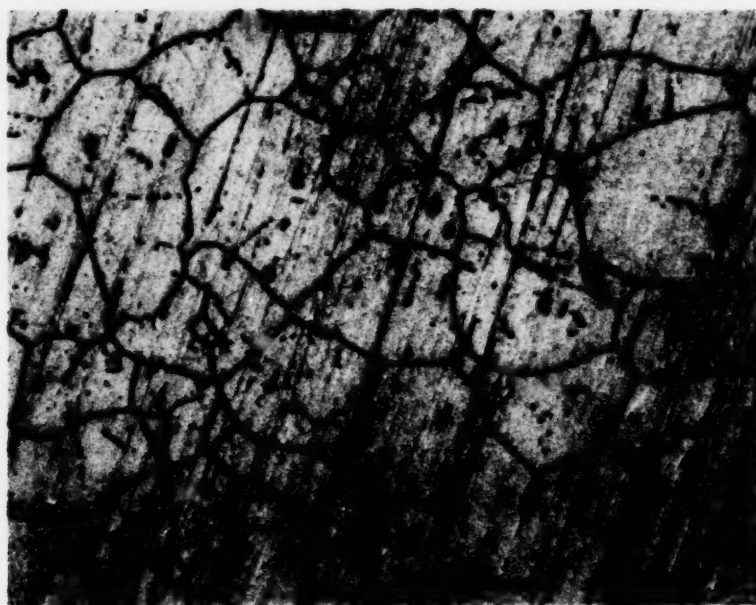


FIGURE A10

INCONEL 600 AFTER CYCLIC POTENTIODYNAMIC
POLARIZATION IN A pH 2.6 DECONTAMINATION
SOLUTION AT 85C (250x)



FIGURE A11

A105 CARBON STEEL AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)



FIGURE A12

LEADED BRONZE AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

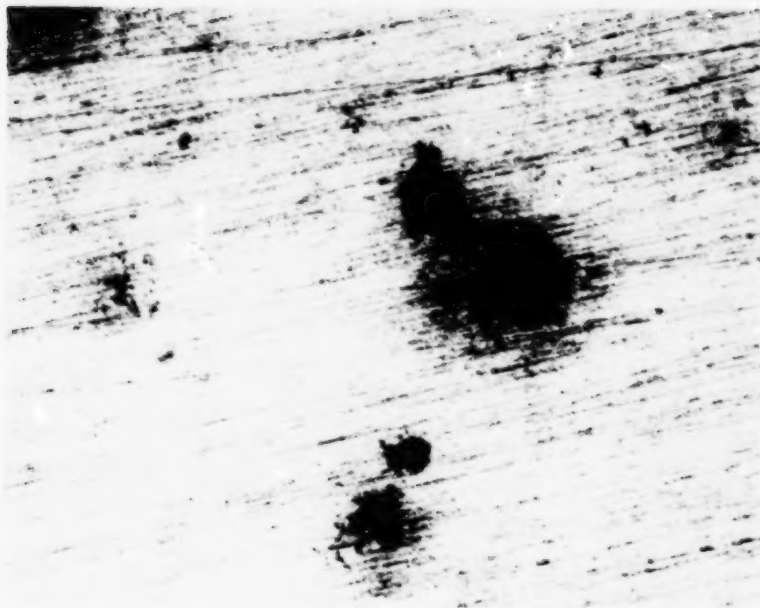


FIGURE A13

403 STAINLESS STEEL AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)



FIGURE A14

410 STAINLESS STEEL AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

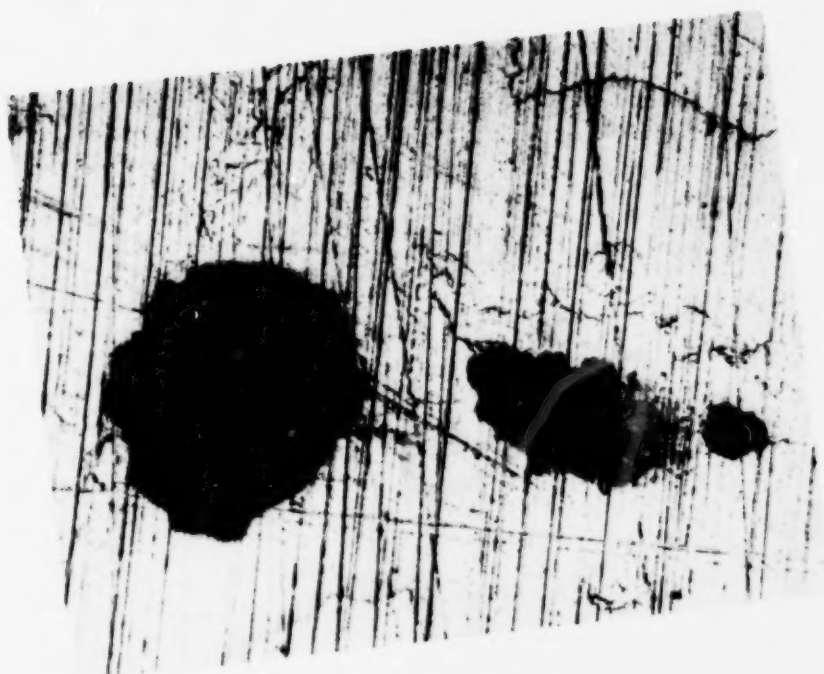


FIGURE A15
MALCOMIZED 17-4PH AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

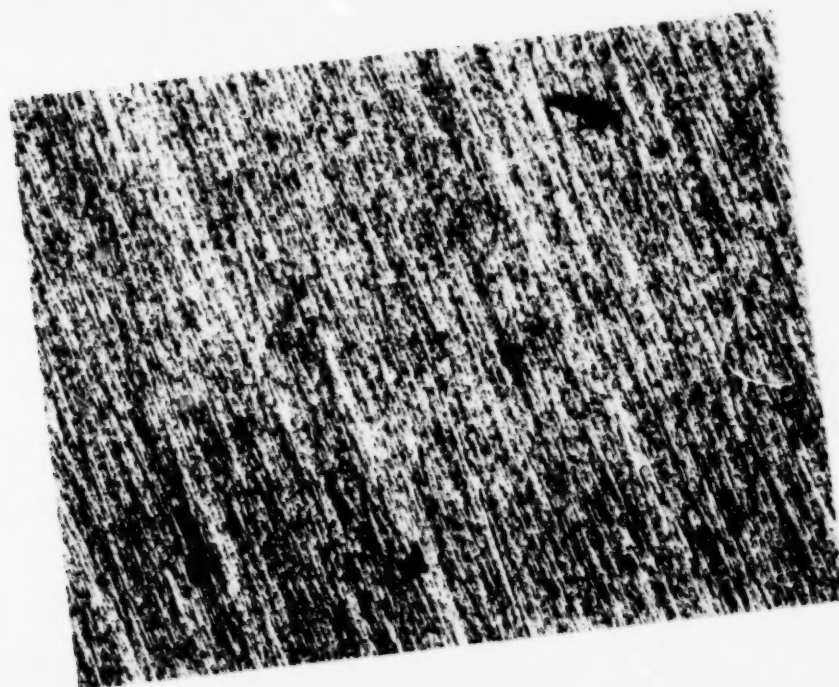


FIGURE A16
NICKEL PLATED 17-4PH AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

171004 RD

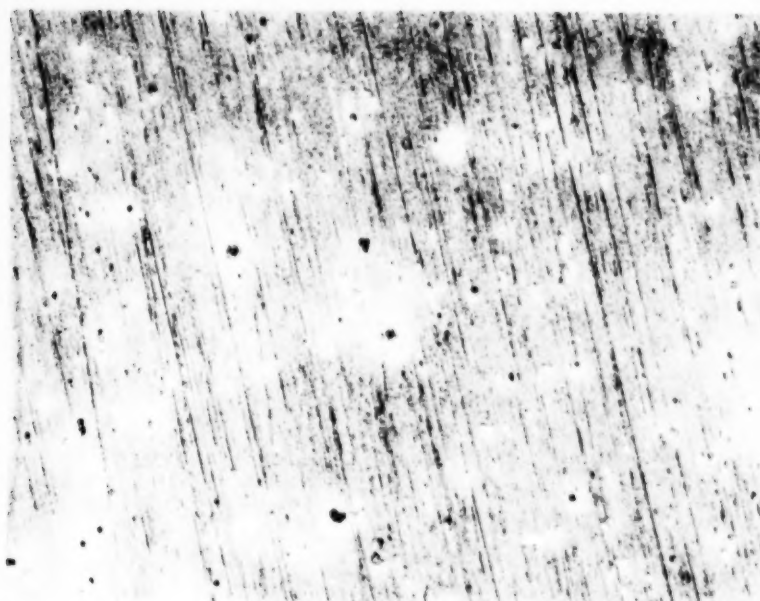


FIGURE A17

ALLOY 17-4PH AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

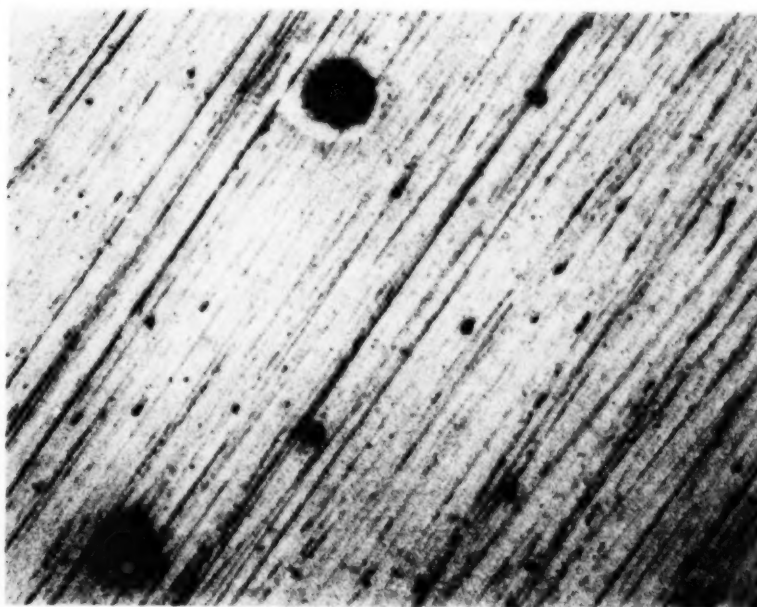


FIGURE A18

INCONEL 600 AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)

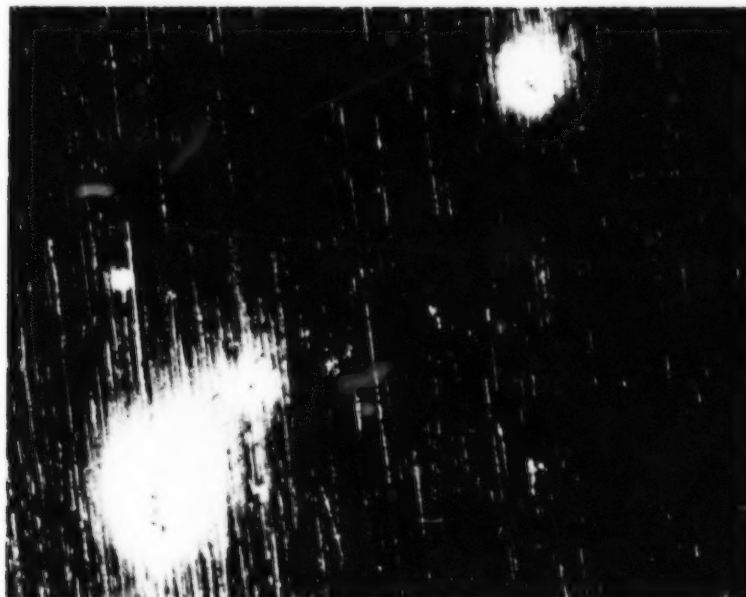


FIGURE A19
MONEL 400 AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)



FIGURE A20
STELLITE 6 AFTER 3.5h IN A pH 1.6
DECONTAMINATION SOLUTION AT 85C (250x)